

SULFURIC ACID EMISSIONS FROM COAL-FIRED BOILERS

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INTRODUCTION

Sulfur trioxide is formed in the furnace and convective pass of coal- and oil-fired boilers; and the rate of formation depends strongly on fuel properties and boiler design and operating conditions. For boilers equipped with SCR reactors for NO_x control, additional amounts of SO_3 are formed in the reactor, with rate of formation depending on parameters such as SCR design and reactor temperature. Once formed, the SO_3 combines with H_2O vapor to form H_2SO_4 vapor in the cold end of the air preheater. The H_2SO_4 leaves a typical coal-fired utility boiler as H_2SO_4 vapor adsorbed or condensed onto fly ash, as H_2SO_4 vapor carried out the stack, and as a liquid deposit trapped on the air preheater baskets. The design and cold end operating conditions of the air preheater govern the fraction of H_2SO_4 which flows from the air preheater with the flue gas.

This paper describes results of calculations, laboratory experiments and field tests, which illustrate how unit operating conditions and air preheater design affect rate of H_2SO_4 emissions.

ACID FORMATION AND DEPLETION PROCESSES

Sulfuric acid begins as small concentrations of sulfur trioxide (SO_3) in the boiler. The SO_3 is formed in the furnace and convective pass of the boiler and in the SCR reactor by the reaction of sulfur dioxide (SO_2) with oxygen. Among the parameters

which influence the amount of SO_3 formation in the boiler are fuel sulfur content, ash content and composition, convective pass surface area, tube metal surface temperature distribution, and excess air level. SO_3 formation in an SCR depends on parameters such as SCR design and reactor temperature. The same fuel burned in two different boilers, but with the same operating conditions, can produce substantially different levels of SO_3 . Further differences occur due to differences in parameters such as load level and amount of excess air.

The SO_3 formation process is complete once the flue gas reaches the air preheater. The SO_3 then leaves a typical coal-fired boiler as a liquid sulfuric acid deposit trapped in the air preheater, as vapor condensed or adsorbed onto fly ash, and as H_2SO_4 vapor and mist carried out the stack.

The air preheater plays an important role in the processes affecting SO_3 and sulfuric acid. In most cases, the gas temperature is reduced within the air preheater from an inlet level of 600 to 700°F to an exit level of about 300°F. During this process, the gas-phase SO_3 reacts with vapor-phase H_2O to form vapor phase H_2SO_4 . By the time the gas flow reaches the cold end of the air preheater, almost all the SO_3 has been transformed to H_2SO_4 .

Condensation of H_2SO_4 and H_2O subsequently occur if the local metal temperatures in the air preheater flow passages drop below the acid dewpoint temperature. Some units are operated with air preheater metal surface temperatures below the dewpoint and others are operated with sufficiently high stack temperatures so no acid condensation occurs. Some of the H_2O and H_2SO_4 vapors are adsorbed or condensed onto the surfaces of the fly ash particles entrained with the flue gas, in the cold end of the air preheater and just downstream of the air preheater exit.

ACID CONDENSATION AND EVAPORATION

Virtually all utility boilers use air preheaters to transfer energy from the hot gases leaving the economizer to the air flowing into the boiler. Two types of air preheaters, the rotary regenerative type and the tubular type are in common use.

A rotating regenerative air preheater is comprised of a rotating metal matrix. As a section of air preheater basket rotates into the duct carrying hot flue gas, heat is transferred from the flue gas to the metal basket material. This heat is then transferred to the cold inlet air as the heated air preheater basket element rotates into the air duct. As a consequence, the basket metal temperature varies circumferentially and with axial position. Changes in inlet air temperature cause the metal temperature distribution to shift upward or downward, thus affecting how much of the air preheater heat transfer surface is below the acid dewpoint temperature. Acid vapor will condense from the flue gas if the heat transfer surface is low enough in temperature. When the resulting condensate is in contact with incoming air, some of the condensate is evaporated and transported back to the furnace by the combustion air. The net rate of condensation of sulfuric acid onto a section of air preheater basket depends upon parameters such as acid concentration in the flue gas, moisture content of inlet air, and how far the basket metal temperature is beneath the dewpoint.

Some utility boilers use large tubular heat exchangers as an alternative to the Ljungstrum design. Similarly to the Ljungstrum case, tubular air preheaters also result in varying amounts of stack gas H_2SO_4 as boiler operating conditions and fuel sulfur content change.

Some acid is adsorbed or condensed onto entrained fly ash in the cold end of the air preheater and in the region just downstream of the air preheater exit. The rates of acid adsorption and condensation vary with parameters such as gas temperature, H_2SO_4 concentration, and fly ash properties. Laboratory measurements of amounts of acid adsorption onto pulverized coal fly ash and calculations of rates of condensation for

those particles below the acid dew point temperature show that adsorption and condensation processes can have a significant impact on gas phase emissions of acid.

IMPACTS OF UNIT OPERATIONS ON STACK EMISSIONS

At many coal-fired units, boiler O₂ levels and stack temperatures vary widely with unit load, with O₂ level increasing and stack temperature decreasing as load is reduced. While the impact of this on SO₃ emissions is highly site specific; in many units, the absolute rate of acid emissions (lb/hr) is significantly higher at minimum load than at full load. The effect of unit load on acid emission rate is due to several factors:

- The excess oxygen concentration at part load is significantly higher than at full load conditions, resulting in higher SO₃ concentrations at the boiler exit.
- The lower flue gas flow rate at part load affects heat and mass transfer within the APH flow passages and, consequently APH acid deposition rate.
- Many units operate with lower stack temperatures at part load.